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(54) **METHODE DE SYNTHESE**
(54) **SYNTHETIC METHOD**

(57) A process to prepare a bulky trialkyl aminophosphonium halide by the reaction of a precursor dihalide with ammonia. The reaction is facile and may be completed under mild reaction conditions. The bulky trialkyl aminophosphonium halides produced by the process of this invention may be utilized in the preparation of ligands for organometallic complexes (preferably using group 4 metals) which are highly active olefin polymerization catalysts. Prior art methods to prepare such organometallic complexes use an azide as an intermediate. Azides require special expertise to handle on a commercial scale and may explosively decompose. The present synthetic method avoids the use of azides.

SYNTHETIC METHOD

ABSTRACT OF THE DISCLOSURE

A process to prepare a bulky trialkyl aminophosphonium halide by the reaction of a precursor dihalide with ammonia. The reaction is facile and may be completed under mild reaction conditions. The bulky trialkyl aminophosphonium halides produced by the process of this invention may be utilized in the preparation of ligands for organometallic complexes (preferably using group 4 metals) which are highly active olefin polymerization catalysts. Prior art methods to prepare such organometallic complexes use an azide as an intermediate. Azides require special expertise to handle on a commercial scale and may explosively decompose. The present synthetic method avoids the use of azides.

FIELD OF THE INVENTION

This invention relates to a novel synthetic method to prepare bulky trialkyl aminophosphonium halides.

BACKGROUND OF THE INVENTION

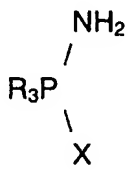
Olefin polymerization catalysts having phosphinimine ligands ("phosphinimine catalysts") are disclosed in co-pending and commonly assigned patent applications. See, for example, Canadian patent applications 2,206,944; 2,210,131; 2,243,783; 2,243,775; and 2,243,726, the disclosures of which are incorporated herein by reference.

The prior art preparation of these phosphinimine catalysts uses an azide as an intermediate as disclosed in the above referenced patent applications. As will be appreciated by those skilled in the art, azides may explosively decompose.

It is an object of this invention to mitigate a problem associated with the prior art preparation of phosphinimine catalysts. We have now discovered a synthetic method which enables the production of phosphinimine catalysts without using an azide.

SUMMARY OF THE INVENTION

In one embodiment, there is provided a process to prepare a molecule defined by the formula:



wherein X is a halogen and each R is an alkyl group, with the proviso that at least one R is selected from isopropyl and cyclohexyl;

wherein said process comprises the reaction of ammonia with a dihalide defined by the formula:

$$R_3PX_2$$

wherein X and each R are as defined above, characterized in that said reaction is undertaken in a protic medium at a temperature of from -40°C to 200°C.

In another embodiment, there is provided a process to prepare tri(tertiary-butyl) Aminophosphonium chloride, wherein said process comprises the reaction of ammonia with tri(tertiary-butyl) phosphonium dichloride.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

The present process is undertaken under very mild conditions. Preferred temperatures are from -40°C to 200°C, most preferably from 20 to 100°C. A positive ammonia pressured of from 1 to 13 atmospheres is also preferred.

It is preferred to use a protic reaction medium, especially ethanol or methanol.

The products of the process of the present invention, namely bulky trialkyl aminophosphonium halides, may be reacted with a base (such as sodium hydroxide, sodium methoxide or butyl lithium) to give a trialkyl phosphinimine $R_3P{=}NH$. The phosphinimine may then be used to prepare the phosphinimine catalysts (described in the above noted patent applications) by reacting it with a metal halide.

The term "bulky trialkyl" refers to the steric bulk of the alkyl substituents on the phosphines atom. As used herein, the term "bulky alkyl" means that the steric bulk should be greater than the steric bulk provided by three phenyl substituents. The use of so-called "Tolman cone angles" is conventionally employed to describe the bulk of phosphines. Triphenyl phosphine is typically described as having a Tolman cone angle of 145° (see, for example, Chemistry of the Elements, by Greenwood and Earnshaw, published by Pergamon Press). The bulky alkyl substituents preferably provide a cone angle (on the precursor phosphine - i.e. the R_3P fragment) of at least 150°, most preferably at least 160°. Exemplary bulky alkyl groups include isopropyl, cyclohexyl, and tertiary butyl. It is particularly preferred that each R group be tertiary butyl.

Further details are provided in the following, non-limited examples.

EXAMPLES

Preparation of Tri-isopropyl Aminophosphonium Bromide, $iPr_3P(NH_2)Br$

To a solution of tri-isopropylphosphine (10g, 62 mmol) in acetonitrile (100 mL) at 0°C was added bromine, Br_2 (3.2 mL, 62 mmol). The reaction was stirred for 1-2 hours and ammonia gas was then added to the reaction flask. An exothermic reaction ensued. After the reaction was complete, the volatiles were removed *in vacuo* to leave a white solid residue. The solid was treated with methylene chloride and then filtered to remove the insoluble NH_4Br by-product. The methylene chloride was removed *in vacuo* to leave the desired product in >95% purity as determined by ^1H

NMR spectroscopy. Yield = 14.6 g, 91%. ^{1}H NMR [200 MHz, $CDCl_3$, δ]: 5.34 (br, s, N*H*$_2$), 2.7 (m, 3H), 1.46 (d, 9H), 1.38 (d, 9H).

Preparation of N-trimethylsilyl Tri-isopropylphosphinimine, $iPr_3P(=N\text{-}SiMe_3)$ from Tri-isopropyl Aminophosphonium Bromide, $iPr_3P(NH_2)Br$

To a slurry of $iPr_3P(NH_2)Br$ (14.4 g, 56 mmol) in THF (250 mL) at ~0°C was added a hexane solution of BuLi (45 mL, 2.5 M., 112.5 mmol). During the addition the $iPr_3P(NH_2)Br$ was observed to dissolve. The reaction was stirred for 60 minutes. It was then added to a solution of trimethylsilyl chloride (10.7 mL, 84 mmol) in THF (200 mL). After 60 minutes the reaction mixture volatiles were removed *in vacuo*. The resulting oily residue was then treated with hexane and the reaction filtered. Removal of the hexane yielded the desired product in >95% purity as determined by ^{1}H NMR spectroscopy. Yield = 13.5g, 98%. ^{1}H NMR [200 MHz, C_7D_8]: 1.61 (m, 3H), 0.97 (d, 9H), 0.87 (d, 9H) 0.28 (s, 9H, Si*Me*$_3$).

Preparation of Tri-*tert*-butylphosphonium dichloride, tBu_3PCl_2, in Ether

To a solution of tBu_3P (5.2 g) in ether (100 ml) at -50°C was slowly added chlorine gas. The reaction was very exothermic and immediately gave a white solid that dissolved as the reaction warmed to 0°C over the one hour chlorine addition period. Once the reaction complete the volatiles were removed *in vacuo*. The resulting white solid product was then isolated as a pure material in quantitative yield. Yield = 7 g. ^{1}H NMR [200 MHz, $CDCl_3$, δ]: 1.79 (d, J = 17.4 Hz)

Preparation of Tri-*tert*-butyl Aminophosphonium Chloride, $tBu_3P(NH_2)Cl$ in Methanol

To a solution of tBu_3PCl_2 (2g) in methanol (30 mL) at 0°C was added ammonia gas at atmospheric pressure. After about 30 minutes it appeared that the solution was saturated with ammonia and the gas addition was terminated. The reaction was then stirred overnight at room temperature. The reaction volatiles were removed *in vacuo* to yield a white solid. ^1H NMR spectroscopic analysis of this solid demonstrated the formation of the desired product although some starting tBu_3PCl_2 remained. Consequently, the solid was redissolved in methanol (30 mL) and the solution placed in a stainless steal pressure vessel. The solution was cooled to -40°C and ammonia (10 g) added. The vessel was then sealed and warmed to 50°C for 16 hours.

^1H NMR analysis of solution at that time revealed that the reaction had gone to completion with only $tBu_3P(NH_2)Cl$ present. Yield = 1.60 g. ^1H NMR [200 MHz, $CDCl_3$, δ]: 5.5 (br, NH_2), 1.55 (d, J = 14.1 Hz, tBu)

Preparation of Tri-*tert*-butyl Aminophosphonium Chloride, $tBu_3P(NH_2)Cl$ in Methanol

To a solution of tBu_3P (2.874 g, 14.2 mmol) in methanol (40 ml) at 0°C was added *tert*-butyl hypochlorite, tBuOCl (1.67 g, 14.2 mmol). After 30 minutes, the volatiles were removed in vacuo from clear reaction mixture and the resulting solid treated with toluene. The toluene was then removed *in vacuo* to leave a white solid. (The toluene was added to help ensure removal of all methanol). The white solid was isolated (yield = 2.88

g) and characterized by ^1H NMR spectroscopy. It was found to contain only tBu_3PCl_2 (~60%) and $tBu_3P=O$ (~40%).

To a solution of the $tBu_3PCl_2/tBu_3P=O$ mixture (2 g) in methanol (30 ml) at -40°C in a stainless steal pressure vessel was added ammonia (5 g). The vessel was sealed and then warmed to 50°C for 64 hours. The reaction was depressurized and the reaction solution transferred to a glass Schlenk vessel. The volatile components were then removed *in vacuo* to leave a white solid. This was treated with methylene chloride and the solution filtered. The methylene chloride was removed *in vacuo* and the resulting solid washed with toluene to remove residual tBu_3PO. The product was then dried *in vacuo*. Yield = 684 mg. ^1H NMR [200 MHz, CD_2Cl_2, δ]: 5.9 (br, NH_2), 1.57 (d, J = 14.1 Hz). The NMR spectrum revealed ~10% residual tBu_3PO remained in the product.

Preparation of N-trimethylsilyl Tri-*tert*-butylphosphinimine, $tBu_3P(=N-SiMe_3)$ from Tri-*tert*-butyl Aminophosphonium Chloride

A sample of $tBu_3P(NH_2)Cl$ (400 mg, 1.6 mmol) contaminated with a small amount of tBu_3PCl_2 was slurried in tetrahydrofuran (30 mL) at -78°C and a solution of BuLi in hexane (1.6 M, 2.2 ml, 3.5 mmol) was added. After 45 minutes, trimethylsilyl chloride (0.4 mL) was added and then the reaction was allowed to warm to room temperature. The reaction mixture volatiles were removed in vacuo to yield a sticky solid. Hexane was added and the reaction filtered. Removal of the hexane gave the desired product as a white solid in >95% purity as determined by ^1H NMR spectroscopy. Yield = 443 mg, 97%. ^1H NMR [200 MHz, C_7D_8, δ]: 1.16 (d, J = 12.7 Hz), 0.33 (s, $SiMe_3$).

COMPARATIVE EXAMPLES

Reaction of tBu_3PBr_2 with Ammonia in Methanol

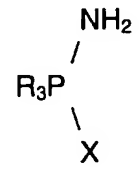
To a solution of tBu_3PBr_2 (1g) in methanol (25 ml) at 0°C was added ammonia gas at atmospheric pressure. After about 30 minutes, it appeared that the solution was saturated with ammonia and the gas addition was terminated. The reaction was then stirred overnight at room temperature. The reaction volatiles were removed *in vacuo* to yield a white solid. ^1H NMR spectroscopic analysis of this solid demonstrated that it consisted primarily of starting material with a large number of other materials. None of these other materials had NMR spectra consistent with $tBu_3P(NH_2)Br$.

Reaction of tBu_3PBr_2 with Ammonia in Acetonitrile

To a solution of tBu_3PBr_2 (2g) in acetonitrile (50 ml) at 25°C was added ammonia gas at atmospheric pressure. Gas addition was continued for 2 hours. The reaction volatiles were removed *in vacuo* to yield a white solid. ^1H NMR spectroscopic analysis of this solid demonstrated that it was starting tBu_3PBr_2.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process to prepare a molecule defined by the formula:



wherein X is a halogen and each R is an alkyl group, with the proviso that at least one R is selected from isopropyl and cyclohexyl;
wherein said process comprises the reaction of ammonia with a dihalide defined by the formula:

$$R_3PX_2$$

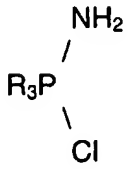
wherein X and each R are as defined above;
characterized in that said reaction is undertaken in a protic medium at a temperature of from -40°C to 200°C.

2. The process of claim 1 wherein each R group is independently selected from isopropyl and cyclohexyl.

3. The process of claim 1 wherein said protic medium is selected from the group consisting of methanol and ethanol and further characterized in that said reaction is undertaken at a pressure of from 1 to 13 atmospheres.

4. The process of claim 1 wherein X is selected form bromine and chlorine.

5. A process to prepare a molecule defined by the formula:



wherein each R is an alkyl group, with the proviso that at least one R is a tertiary butyl group, and wherein said process comprises the reaction of ammonia with a dichloride defined by the formula:

R_3PCl_2

wherein each R is as defined above.

6. A process to prepare tri(tertiary-butyl) Aminophosphonium chloride, wherein said process comprises the reaction of ammonia with tri(tertiary-butyl) phosphonium dichloride at a pressure of from 1 to 13 atmospheres and a temperature of from -40°C to 200°C.

7. The process of claim 6 wherein completed in a protic solvent.